

1 **PROCESS FOR REMOVING CONTAMINANTS FROM**
2 **FISCHER-TROPSCH FEED STREAMS**

3
4
5 FIELD OF THE INVENTION

6
7 This invention relates to a process for removing filterable particulates and
8 un-filterable aluminum-containing contaminants from a Fischer-Tropsch feed
9 stream.

10
11 BACKGROUND OF THE INVENTION

12
13 The majority of fuel today is derived from crude oil. Crude oil is in limited
14 supply, and fuel derived from crude oil tends to include nitrogen-containing
15 compounds and sulfur-containing compounds, which are believed to cause
16 environmental problems such as acid rain.

17
18 Natural gas is abundant and may be converted into hydrocarbon fuels,
19 lubricating oils, chemicals, and chemical feedstocks. One method for
20 producing such products from natural gas involves converting the natural gas
21 into synthesis gas ("syngas") which is a mixture primarily of hydrogen and
22 carbon monoxide. In the Fischer-Tropsch process, the syngas produced from
23 a natural gas source is converted into a product stream that includes a broad
24 spectrum of products, including gases, such as, propane and butane; a liquid
25 condensate which may be processed into transportation fuels; and wax which
26 may be converted into base oils as well as lower boiling products, such as,
27 diesel. The conversion of the wax and condensate usually involves passing
28 the feed downwardly along with a co-current hydrogen enriched gas stream
29 through a catalyst bed contained in one or more hydroprocessing reactors
30 (i.e., a downflow reactor). The liquid hydrocarbon feed "trickles" down through
31 the catalyst beds in the hydroprocessing reactor and exits the reactor bottom
32 after the desired upgrading is achieved.

1 The Fischer-Tropsch feed stream as recovered from the Fischer-Tropsch
2 reactor may contain filterable particulate contaminants, such as, for example,
3 catalyst fines and rust and scale derived from the equipment. In addition, in
4 some instances, un-filterable aluminum-containing contaminants have been
5 found in the feed stream which cannot be removed using conventional
6 particulate recovery methods. These un-filterable aluminum contaminants will
7 coalesce into particulates under the conditions prevailing in the
8 hydroprocessing reactor and can cause serious operating difficulties in a
9 fixed-bed, trickle-flow hydroprocessing reactor. The most frequent difficulty is
10 pressure drop build-up and eventual plugging of the flow-paths through the
11 catalyst beds as the catalyst pellets filter out the feed particulates. Such
12 build-up can cause significant economic loss in lost production and
13 replacement catalyst costs. These non-filterable aluminum-containing
14 contaminants usually will concentrate in the heavier wax fraction of the
15 Fischer-Tropsch product stream. U.S. Patent No. 6,359,018 describes an
16 upgrading process in which the Fischer-Tropsch feed stream passes in
17 up-flow mode through the hydroprocessing reactor and is then filtered to
18 remove the particulates.

19
20 There are two types of up-flow operation which may be used in carrying out
21 the present invention, fixed bed and ebullating bed operation. When a fixed
22 bed reactor is operated in up-flow mode, there is little or no expansion of the
23 catalyst bed during operation. It should be understood that since the reactor
24 walls are rigid, the expansion of the catalyst bed will take place only along the
25 vertical axis of the bed. Thus, when referring to bed expansion in this
26 disclosure, the increase in height of the bed or depth of the bed in the reactor
27 is an appropriate measure of bed expansion and is directly related to volume.
28 An ebullating bed also employs the upward flow of feedstock, however, an
29 ebullating bed differs from an up-flow fixed bed in that the upward flow in the
30 ebullating bed is sufficient to suspend the catalyst and create random
31 movement of the catalyst particles. During operation the volume of an
32 ebullating bed will expand, usually by at least 20 percent, as compared to the

1 volume of catalyst in the reactor when there is no flow of hydrogen and
2 feedstock through the bed.

3
4 Up-flow fixed bed operation and ebullating bed operation differ from fluidized
5 bed operation which is not used in the carrying out the present invention.
6 In fluidized bed operation finely divided solid catalyst particles are lifted and
7 agitated by a rising stream of process gas. In a fluidized bed the catalyst
8 particles are suspended or entrained in the rising gas stream. A fluidized bed
9 is sometimes referred to as a boiling bed due to its appearance to a boiling
10 liquid. Bed expansion in a fluidized bed is considerably greater than observed
11 in an ebullating bed.

12
13 It would be advantageous to provide an efficient process for removing both
14 the filterable and un-filterable contaminants from the Fischer-Tropsch feed
15 stream prior to the downstream hydroprocessing operations. The present
16 invention provides such a process.

17
18 As used in this disclosure the word "comprises" or "comprising" is intended as
19 an open-ended transition meaning the inclusion of the named elements, but
20 not necessarily excluding other unnamed elements. The phrase
21 "consists essentially of" or "consisting essentially of" is intended to mean the
22 exclusion of other elements of any essential significance to the composition.
23 The phrase "consisting of" or "consists of" is intended as a transition meaning
24 the exclusion of all but the recited elements with the exception of only minor
25 traces of impurities.

26 27 SUMMARY OF THE INVENTION

28
29 The present invention is directed to a process for removing contaminants from
30 the products of a Fischer-Tropsch synthesis reaction, said contaminants
31 comprising (i) particulates having an effective diameter of greater than
32 1 micron and (ii) at least 5 ppm of aluminum in aluminum-containing
33 contaminants having an effective diameter of less than 1 micron, said process

1 comprising the steps of (a) passing the products of the Fischer-Tropsch
2 synthesis reaction through a first particulate removal zone capable of
3 removing particulates having an effective diameter of greater than 1 micron;
4 (b) collecting from the first particulate removal zone a substantially particulate
5 free Fischer-Tropsch feed stream containing 5 ppm or more of aluminum in
6 aluminum containing-contaminants having an effective diameter of less than
7 about 1 micron; (c) contacting the substantially particulate free Fischer-
8 Tropsch feed stream in up-flow mode with an aluminum active catalyst in a
9 guard-bed under aluminum activating conditions, whereby a feed stream
10 mixture is formed which comprises aluminum-containing particles having an
11 effective diameter of more than 1 micron in a Fischer-Tropsch hydrocarbon
12 continuous phase; (d) passing the feed stream mixture through a second
13 particulate removal zone capable of removing substantially all of the
14 aluminum-containing particles formed in step (c); and (e) recovering from the
15 second particulate removal zone a Fischer-Tropsch product containing less
16 than about 5 ppm total aluminum.

17
18 As used in this disclosure the term aluminum active catalyst refers to a
19 catalyst which under the conditions prevailing in the guard-bed will lead the
20 aluminum contaminants to coalesce into particulates having an effective
21 diameter of about 1 micron or greater. Most aluminum active catalyst will
22 contain at least one active Group VI metal, such as chromium, molybdenum,
23 and tungsten, and at least one active Group VIII base metal, such as nickel or
24 cobalt. An active metal is a metal within Group VI or Group VIII of the periodic
25 table of the elements (Chemical Abstract Services) which has the ability,
26 either as the elemental metal or as a compound of the metal, to catalyze the
27 formation of the particles containing the aluminum.

28
29 It has been found that the un-filterable aluminum contaminant is usually
30 concentrated in the higher molecular weight fractions of the Fischer-Tropsch
31 product stream. The products from Fischer-Tropsch reactions generally will
32 include a light reaction product and a waxy reaction product. The light
33 reaction product, referred to as the condensate fraction, includes

1 hydrocarbons boiling below about 700 degrees F (e.g., tail gases through
2 middle distillates) largely in the C₅ to C₂₀ range, with decreasing amounts up
3 to about C₃₀. The waxy reaction product, referred to as the wax fraction,
4 includes hydrocarbons boiling above about 600 degrees F (e.g., vacuum gas
5 oil through heavy paraffins), largely on the C₂₀₊ range, with decreasing
6 amounts down to about C₁₀.

7
8 Although the process of the invention may be used with any type of
9 Fischer-Tropsch reactor design, the invention is particularly advantageous
10 when used with a slurry-type reactor where the wax fraction and the
11 condensate fraction are recovered separately from the condensate fraction.
12 Consequently, the wax fraction from the slurry reactor will contain the majority
13 of the un-filterable aluminum.

14
15 As already noted, at least some of the aluminum contaminant in the
16 Fischer-Tropsch feed stream is in a form which cannot be readily removed by
17 using filtration or other common methods for removing particulates from a
18 liquid. Therefore, when this disclosure refers to an aluminum-containing
19 contaminant having an effective diameter of less than 1 micron what is being
20 referred to is an aluminum contaminant which may be in the form of a soluble
21 aluminum compound, colloidal particles, or ultra-fine particulates. An effective
22 diameter of 1 micron was selected as the distinguishing characteristic of the
23 aluminum contaminant, because particles smaller than 1 micron generally are
24 not capable of removal using conventional commercial filtering methods which
25 are suitable for use with liquid hydrocarbons. Consequently, the aluminum
26 contaminants are in a form which cannot be removed by a filter having an
27 effective porosity of about 1 micron. While filtering is the preferred method for
28 removing particles from both the Fischer-Tropsch feed stream and the feed
29 stream mixture exiting the guard-bed when practicing the invention, other
30 methods such as centrifugation or distillation may also be employed, if so
31 desired.

1 An important aspect of the present invention is the operation of the guard-bed
2 reactor in up-flow mode. An up-flow reactor differs from the typical down-flow
3 fixed bed reactor due to the upward flow of fluid in the reactor. Operation of
4 the reactor in up-flow mode is advantageous in the present invention, since
5 the up-flow reactor has a lower pressure drop and a greater resistance to
6 pressure drop buildup than a conventional down-flow reactor. The guard-bed
7 may be operated as either an up-flow fixed bed or as an ebullating bed. In a
8 fixed bed, i.e., one where there is relatively little movement of the catalyst
9 particles, the flow of fluid upward through the catalyst bed is low enough to
10 minimize the expansion of the catalyst bed as compared to the bed volume
11 when no fluid is passing through the bed. The expansion of the fixed catalyst
12 bed in an up-flow reactor when used with the present invention generally will
13 not exceed 5 percent and preferably will not exceed 2 percent. Since the
14 up-flow fixed bed reactor does not require as large a volume as an ebullating
15 bed using the same amount of catalyst, the up-flow fixed bed is generally
16 preferred.

17

18 Hydrogen should be present in the guard-bed and usually mixed with the
19 filtered Fischer-Tropsch feed stream entering the guard-bed. In coalescing
20 the aluminum contaminants in the guard-bed, temperatures of about
21 550 degrees F or higher are most effective. Temperatures of about
22 600 degrees F or higher are preferred, and temperatures of 650 degrees F
23 are especially preferred. In general, the higher the space velocity in the
24 guard-bed the higher the temperature in the guard-bed should be to assure
25 the coalescence of substantially all of the aluminum contaminants. The
26 Fischer-Tropsch product recovered from the second particulate removal zone
27 should contain less than about 5 ppm of aluminum expressed as elemental
28 metal and preferably should contain less than about 2 ppm aluminum as
29 elemental metal. Especially preferred is a Fischer-Tropsch product containing
30 1 ppm total aluminum or less when expressed as elemental metal.

1 BRIEF DESCRIPTION OF THE DRAWING

2
3 The Figure is a schematic representation in block diagram form of one
4 embodiment of the invention.

5
6 DETAILED DESCRIPTION OF THE INVENTION

7
8 The present invention will be more clearly understood by referring to the
9 Figure. Syngas 2 comprising a mixture of carbon monoxide and hydrogen is
10 introduced into the Fischer-Tropsch reactor 4 where the mixture of carbon
11 monoxide and hydrogen contacts a Fischer-Tropsch catalyst to yield a mixture
12 of products ranging from methane to C₁₀₀₊ hydrocarbons. In the Figure, the
13 heavier products 6 from the Fischer-Tropsch synthesis, which comprise
14 primarily hydrocarbons boiling above about 600 degrees F, are shown being
15 recovered separately from the lower molecular weight products 8, which
16 comprise primarily hydrocarbons boiling below about 700 degrees F.
17 In commercial practice the lower molecular weight hydrocarbons will be
18 further separated (not shown in the Figure) into a gaseous fraction and a
19 liquid condensate. The heavy products 6, which are often referred to as
20 Fischer-Tropsch wax, contain both filterable particulates and un-filterable
21 aluminum-containing contaminants. The particulates which are generally
22 larger than 1 micron in diameter, are removed from the wax stream by the first
23 product filter 10. In the Figure, the first product filter is shown for clarity as
24 located in line 6, however, in an alternative embodiment the first product filter
25 may be located within the Fischer-Tropsch reactor 4. In addition, the first
26 product filter may actually consist of a series of several filters, within the
27 reactor, outside the reactor, or both. The filtered wax stream in line 12, which
28 is now substantially free of particulates, has been found to still contain a
29 significant amount of an aluminum-containing contaminant. The filtered wax
30 stream 12 is sent along with hydrogen gas entering via line 11 in up-flow
31 mode to the guard-bed reactor 14 which contains an aluminum active catalyst
32 and is maintained at a temperature of about 550 degrees F or higher. Under
33 the conditions prevailing in the guard-bed reactor, the aluminum-containing

1 contaminant will coalesce into particles having an effective size greater than
2 about 1 micron. Due to the up-flow mode in the guard-bed, the presence of
3 the particles forming in the Fischer-Tropsch wax will not plug up the catalyst
4 bed. A mixture comprising the Fischer-Tropsch wax which makes up a
5 continuous liquid phase and a discontinuous phase comprising suspended
6 aluminum-containing particles is collected from the top of the guard-bed by
7 line 16 and carried to the second product filter 18. The second product filter
8 removes the aluminum-containing particles formed in the guard-bed from the
9 wax stream and yields a purified wax feed stream containing less than 5 ppm
10 aluminum as elemental metal. The purified wax feed stream passes by way
11 of line 20 to a conventional down-flow hydroprocessing reactor, such as a
12 hydrotreating unit or a hydrocracking unit. The hydroprocessed product
13 stream is shown leaving the hydroprocessing reactor via line 24.

14

15 Depending on the type of Fischer-Tropsch reactor or the down-stream
16 processing scheme, the wax fraction and the liquid condensate may be
17 recovered from the Fischer-Tropsch reactor as a single product stream. In
18 the embodiment shown in the drawing, the wax fraction will have a relatively
19 high viscosity, therefore, it may be advantageous to use a different method for
20 removing the particulates, such as, for example, by centrifugation. In an
21 alternate embodiment, all or part of the condensate may be blended with the
22 wax fraction to lower the viscosity of the heavier Fischer-Tropsch product 6
23 making the filtering steps easier.

24

25 The guard-bed used in the present invention differs from guard-beds taught in
26 the prior art in at least two important respects. In the present process the
27 guard-bed is not intended to actually trap the contaminants in the feed. Also,
28 unlike processes in the prior art, such as the process disclosed in U.S. Patent
29 No. 6,359,018, the reaction taking place in the guard-bed reactor is not
30 intended as an upgrading step. The primary purpose of the guard-bed is to
31 coalesce the aluminum-containing contaminant into filterable particles.
32 Although base metal hydrotreating catalyst may serve as aluminum active
33 catalyst, the catalyst and the reaction conditions present in the guard-bed are

1 not necessarily the same as employed in a hydroprocessing operation, such
2 as, hydrotreating or hydrocracking processes. For example, palladium is
3 present as an active metal in many catalysts intended for hydroprocessing
4 operations, such as, hydrocracking and hydroisomerization. However,
5 palladium has been found to be inactive when used as a guard-bed catalyst in
6 the present invention. Preferred catalysts for use in the present invention
7 contain an aluminum active metal comprising at least one active Group VI
8 metal and at least one active Group VIII base metal. Preferred Group VI
9 metals are selected from the group consisting of chromium, molybdenum, and
10 tungsten. Preferred Group VIII base metals are selected from the group
11 consisting of nickel and cobalt. Catalysts containing molybdenum, nickel, and
12 phosphorous have been found to be suitable for carrying out the reaction in
13 the guard-bed.

14

15 The matrix component of the catalyst can be of many types including alumina,
16 silica, or those having acidic catalytic activity. Ones that have activity include
17 amorphous silica-alumina or may be a zeolitic or non-zeolitic crystalline
18 molecular sieve. Examples of suitable matrix molecular sieves include
19 zeolite Y, zeolite X and the so-called ultra stable zeolite Y and high structural
20 silica:alumina ratio zeolite Y such as that described in U.S. Patent
21 Nos. 4,401,556; 4,820,402 and 5,059,567. Small crystal size zeolite Y, such
22 as that described in U.S. Patent No. 5,073,530, can also be used.

23 Non-zeolitic molecular sieves which can be used include, for example,
24 silicoaluminophosphates (SAPO), ferroaluminophosphate, titanium
25 aluminophosphate, and the various ELAPO molecular sieves described in
26 U.S. Patent No. 4,913,799 and the references cited therein. Details regarding
27 the preparation of various non-zeolite molecular sieves can be found in
28 U.S. Patent Nos. 5,114,563 (SAPO); 4,913,799 and the various references
29 cited in U.S. Patent No. 4,913,799. Mesoporous molecular sieves can also be
30 used, for example the M41S family of materials (*J. Am. Chem. Soc.* 1992,
31 114, 10834-10843), MCM-41 (U.S. Patent Nos. 5,246, 689; 5,198,203 and
32 5,334,368), and MCM-48 (Kresge et al., *Nature* 359 (1992) 710). The

1 contents of each of the patents and publications referred to above are hereby
2 incorporated by reference in its entirety.

3
4 Suitable matrix materials may also include synthetic or natural substances as
5 well as inorganic materials such as clay, silica and/or metal oxides such as
6 silica-alumina, silica-magnesia, silica-zirconia, silica-thoria, silica-beryllia,
7 silica-titania as well as ternary compositions, such as silica-alumina-thoria,
8 silica-alumina-zirconia, silica-alumina-magnesia, and silica-magnesia zirconia.
9 The latter may be either naturally occurring or in the form of gelatinous
10 precipitates or gels including mixtures of silica and metal oxides. Naturally
11 occurring clays which can be composited with the catalyst include those of the
12 montmorillonite and kaolin families. These clays can be used in the raw state
13 as originally mined or initially subjected to calcination, acid treatment or
14 chemical modification.

15
16 The catalyst particles must be of an appropriate size so that the particles
17 formed by the coalescence of the aluminum contaminant do not plug up the
18 guard-bed and that diffusion limitations and reactor pressure drops are
19 minimized. The catalyst particles will generally have a cross sectional
20 diameter between about 1/64 inch and about 1/2 inch, and preferably between
21 about 1/32 inch and about 1/4 inch, i.e., the particles will be of a size to be
22 retained on a 1/64 inch, and preferably on a 1/32 inch screen and will pass
23 through a 1/2 inch, and preferably through a 1/4 inch screen. The catalyst
24 particles may have any shape known to be useful for catalytic materials,
25 including spheres, cylinders (i.e., extrudates), fluted cylinders, prills, granules
26 and the like. Preferred catalyst particles have a cross sectional diameter of at
27 least 1/20 inch (i.e., the particles will be of a size to be retained on a 1/20 inch
28 screen) and have a spherical or cylindrical shape.

29
30 The superficial velocity of the liquid flowing upwards through the
31 hydroprocessing reactor(s) is maintained at a rate greater than the settling
32 velocity of the particulate contaminants forming in the upward flowing liquid,
33 but preferably less than the fluidization velocity of the catalyst particles in the

1 reactor(s). Such values of fluid velocity are based on the size, shape and
2 density of the particulate contaminants and of the catalyst particles, and
3 therefore depends on the specific processing configuration employed.
4 Methods for calculating such velocities are well within the capability of one
5 skilled in the art. In general, a liquid hourly space velocity (LHSV) in the
6 guard-bed of about 1 or greater is preferred. However, as the space velocity
7 increases, the temperature in the guard-bed must also increase to achieve the
8 same efficiency in coalescing the aluminum contaminant.

9
10 Temperatures of about 550 degrees F or higher are generally preferred in the
11 guard-bed with temperatures of about 600 degrees F or more being preferred.
12 Temperatures above 650 degrees F are generally preferred at a space
13 velocity above 1 LHSV. The optimal temperature will be that temperature
14 which leads to the coalescence of substantially all of the aluminum-containing
15 contaminants present in the product when using the selected active aluminum
16 catalyst with the space velocity at which the guard-bed is operated. Following
17 treatment in the guard-bed, the product ideally should contain no more than
18 5 ppm, preferably 2 ppm or less, and most preferably 1 ppm or less of
19 aluminum measured as elemental metal.

20
21 The removal of the aluminum containing particles in the second particulate
22 removal zone will usually be accomplished by filtration. However, other
23 methods for removing the particulates, such as centrifugation or distillation
24 may also be used if desired. Regardless of the method employed
25 substantially all of the particulates present in the liquid should be removed to
26 protect the downstream hydroprocessing reactors from being plugged up.
27 By employing the process of the invention a Fischer-Tropsch feed stream is
28 produced which may be readily upgraded using conventional hydroprocessing
29 methods without the disadvantage of having contaminants plug the reactors.

30
31 The following examples are intended to further illustrate the invention, but are
32 not to be construed as limitations on the scope of the invention.

EXAMPLES

Example 1

A Fischer-Tropsch wax prepared using a cobalt based catalyst was filtered to remove particulates having an effective diameter of about 1.2 microns or greater. The aluminum content of the filtered wax was determined. The filtered Fischer-Tropsch wax was mixed with hydrogen and passed up-flow through a guard-bed containing an active catalyst. This catalyst contained 1.6 weight percent nickel, 6.5 weight percent molybdenum, and 1.4 weight percent phosphorous on an alumina base and was presulfided before starting the Fischer-Tropsch feed. The process conditions were 290 PSIG total pressure, hydrogen recycle gas rate of 1200 SCF gas per barrel of liquid feed, liquid hourly space velocities of 1 and 2, and at catalyst temperatures ranging between 290 degrees F and 650 degrees F. The treated Fischer-Tropsch wax was filtered a second time using a 1.2 micron filter. The filtered product was analyzed for aluminum content. The results are shown in Table 1 below.

Table 1

Test #	LHSV	Temp. °F	Al ppm in Feed ¹	Al ppm in Product ²
1	1	450	16.8	12
2	1	550	16.8	3.9
3	1	625	16.8	0.6
4	2	600	16.8	9
5	2	625	16.8	3.1
6	2	650	16.8	0.5

¹ Aluminum content expressed as elemental metal present in the filtered feed to the guard-bed.

² Aluminum content expressed as elemental metal present in the product recovered from the second filter step.

It will be noted that at a space velocity of 1 LHSV a temperature of 550 degrees F was necessary to lower the aluminum content of the Fischer-Tropsch product to less than 5 ppm. To lower the aluminum content

below 1 ppm a temperature of 625 degrees F was required (Test #2).
At a space velocity of 2 LHSV a temperature of 650 degrees F was needed
(Test #6). As the space velocity increases, the temperature must also
increase to achieve acceptable levels of aluminum in the product.

Example 2

The experiment of Example 1 was repeated using five different
Fischer-Tropsch wax fractions containing various levels of aluminum
contaminants. Liquid hourly space velocities for the tests ranged between 1
and 3. The results are shown in Table 2.

Table 2

Wax Sample	Test #	LHSV	Temp. °F	Al ppm in Feed ¹	Al ppm in Product ²
A	7	2.0	675	18	0.7
B	8	2.0	675	43.8	0.7
B	9	2.0	650	43.8	15.0
B	10	3.0	675	43.8	16.0
B	11	3.0	700	43.8	1.8
C	12	3.0	600	43.9	36.0
C	13	2.0	675	43.9	3.9
C	14	2.0	680	43.9	4.1
D	15	2.0	690	48.7	1.6
D	16	1.5	690	48.7	1.8
D	17	1.0	690	48.7	1.2
E	18	1.0	690	44.1	1

¹ Aluminum content expressed as elemental metal present in the filtered feed to the guard-bed.

² Aluminum content expressed as elemental metal present in the product recovered from the second filter step.

The results shown in Table 2 generally support the conclusions drawn from the data in Table 1. Note that in order to achieve less than 5 ppm of aluminum at a LHSV of 2.0 or higher, a temperature of 675 degrees F is required. At higher space velocities the efficiency of the catalyst to coalesce the aluminum contaminant decreases.